Examination of Plasma Spray Parameters for $YBa_2Cu_3O_{7-x}$ Coatings†

Akira OHMORI*, Shougo SHIMOMIYA, Fumio KAWAKAMI** and Nobuya IWAMOTO****

Abstract

This paper examines the influences of plasma spray parameters on property and structure of $YBa_2Cu_3O_{7-x}$ coatings produced by air plasma spraying using calcinated superconducting $YBa_2Cu_3O_{7-x}$ powder and raw material spray dried powders of Y_2O_3, $2BaCO_3$ and 3CuO.

As plasma spray parameters, plasma arc power, plasma gas flow rates, kind of gasses and standoff distance were adopted. In order to obtain a superconducting coating uniformly and easily by appropriate thermal treatment, it was important to suppress the decomposition of powder through plasma jet, so that it was necessary to select plasma spray conditions of lower heat content for the superconducting powders. On the other hand, it was important to facilitate the mutual reaction among 3 kinds of oxides during plasma spraying and to increase heat content for the agglomerated powders.

KEY WORDS : (Plasma spraying) (Spray parameter) ($YBa_2Cu_3O_{7-x}$) (Coating) (Superconductivity)

1. Introduction

A number of investigations for processing and properties of superconducting coatings produced by plasma spray techniques have been reported.[1-12] Most of them described for properties of coatings thermally treated relatively at high temperature and for long time. However, there were a few that discussed the influences of plasma spray parameters on as-deposited compositions. To spread the applications of this process which has resulted in a number of advantages such as processing in atmosphere, high deposition rate, less restriction in thickness, shapes and so on, it is important to make problems clear for applying plasma spraying process to the formation of superconducting coatings.

On this process, it is recognized that the thermal effect is excessive, momentary and different particle by particle during plasma spraying, so that it is not easy to maintain characteristics without any decomposition of structure and disruption of phase throughout the course of deposition especially for superconducting powders. Then, a post thermal treatment has been applied to provide superconductivity. As a superconductor, generally, the coating requires high density and uniformity for good electric and magnetic properties, however, a dense coating usually requires high power operations and post thermal treatment after spraying. Therefore, considering plasma spray process as a pre-forming step, except the matter of density, and to abbreviate thermal treatment, the influences of spray parameters on transformation of compositions were investigated using superconducting powders and non-reacted agglomerated powders.

2. Materials and Experimental procedure

$YBa_2Cu_3O_{7-x}$ superconducting powders were prepared by the solid state reaction method. Agglomerated powders were prepared by conventional spray-dried method with Y_2O_3, $BaCO_3$, and CuO reagents (Y : Ba : Cu = 1 : 2 : 3). SEM photographs and XRD results of each powder are shown in **Fig. 1**. The deposits were produced with Metco 9MB and 3APG plasma spray torches, and formed over 0.3mm thickness on a thin blasted stainless sheet. Then it was carefully twisted for deposits to be removed from substrate and they were thermally treated at 1223K for 0min, 2hrs, 6hrs in air and cooled in the furnace. At first, the influence of plasma power, arc current and voltage respectively, were examined by using Ar mono gas as plasma and powder carrier gas. Then a kind of gas, a volume of plasma gas and standoff distance were examined.

Plasma spray conditions used in this experiment are shown in **Table 1**.

All deposits, sprayed and thermally treated, were

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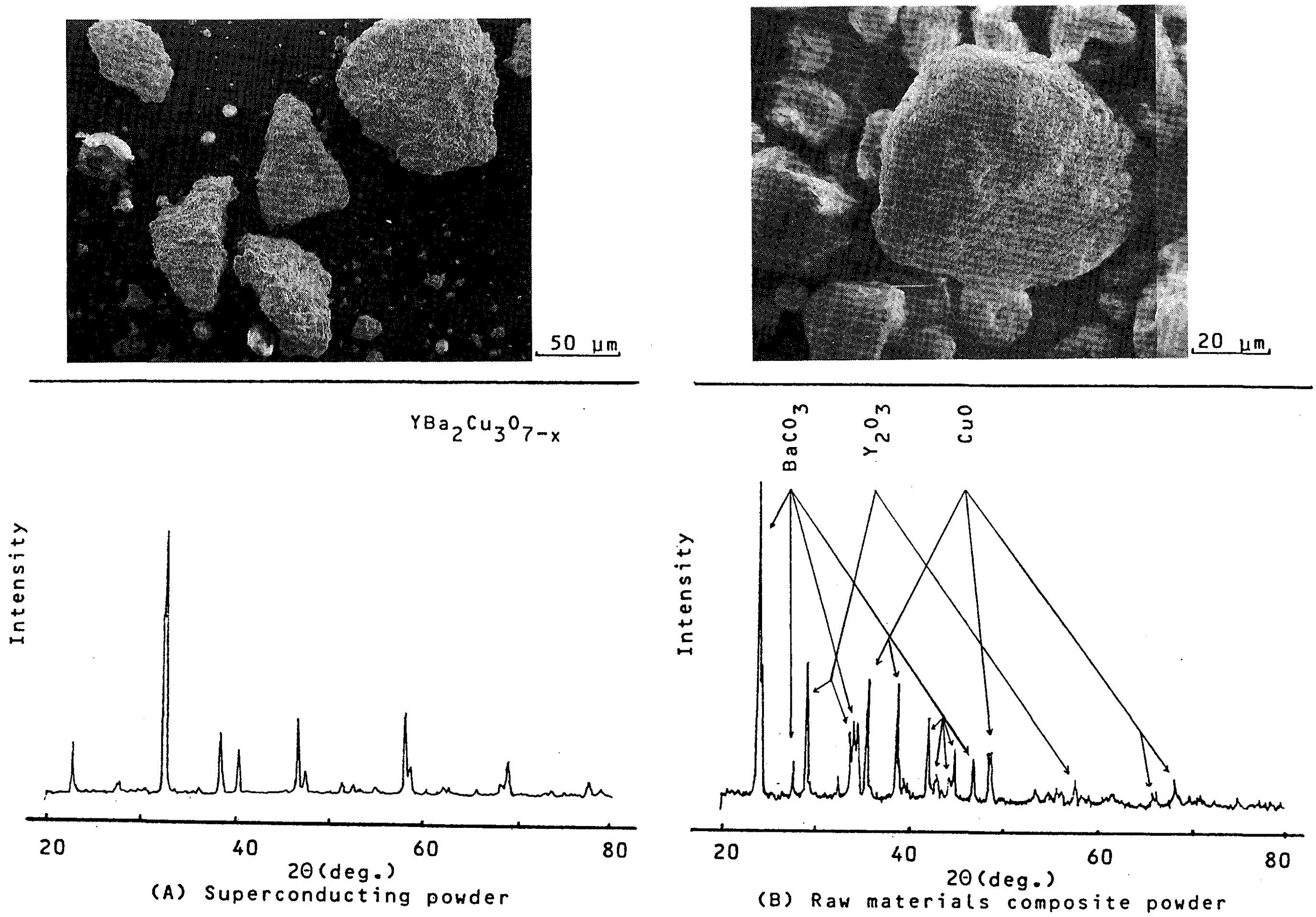

Fig. 1 SEM photographs and XRD patterns of spray powders.

exmined by SEM, EDX and X-ray diffraction. And superconducting properties of thermally treated deposits were examined by resistivity measurement(Tc) carried out by a four-probe method.

3. Results and Discussion

3.1 Effect of plasma power on Tc of deposits

Figure 2 shows the effect of plasma power and thermal treatment on the XRD patterns and Tc of plasma sprayed deposits produced under plasma spray conditions in Table 1. with superconducting powders.

From X-ray diffraction patterns of as-deposited coatings of superconducting powders showed the presence of Y_2O_3 and other uncertain broad peaks, and there was a tendency that this broad peaks become dominant with increase of plasma power. When deposit was produced at 80volts(40KW), non of $YBa_2Cu_3O_{7-x}$ peak appeared, but the peak becomes dominant for 30volt(13.5KW) on the contrary. Those deposits less decomposed recover easily superconductivity by heat treatment for short time. But in certain cases, no recovery was observed for those deposits. From these results, it was proved that plasma flame at high plasma power decomposed severely $YBa_2Cu_3O_{7-x}$ powders and where increase of arc voltage was more remarkable for the decomposition than that of arc current. This tendency was observed also in Tc measurement results of thermally treated coatings as shown in Fig. 2.

In the **Fig. 3**, similar results for the agglomerated powders were shown.

This figure shows that when the deposits were prepared by plasma spraying with the powders, the reaction among three kind of oxides became easier during plasma spraying with higher power than that with lower plasma power to give easily superconductive deposits by heat treatment in air. Results of EDX element analysis of as-deposited and thermally treated coatings are shown in **Fig. 4**.

From this figure, it can be seen that the uniform superconductive deposits were formed by heat treatment at 1223K for 2hr in air.

Table 1 Spray parameters and physical parameters of plasma jet.

	Arc current			Arc voltage			Plasma gas		Gas flows, S/D	
Torch	9 M B			3 APG			9 MB		3 APG	
Plasma gas	Ar			Ar			Ar/H2	N2	Ar	
Amp/Vol	450x30	650x30	850x36	500x40	500x60	500x80	500x76	500x80	450x62	300x55
Input power KW	13.5	19.5	30.6	20.0	30.0	40.0	33.0	40.0	27.7	16.5
Nozzle type	732			310			732	730	300	
Powder port	#3-6			#2			#2		#5	
S/distance mm	60~150			125			140		115	90
Orifice s mm²	47.8			50.3			47.8		15.9	
Flows V_a SLM	40.0			55.0			48.0		70.0	
velocity v M/s	13.94			18.22			16.73		73.38	
D_E J/cc	20.2(1)	29.2(2)	45.9	24.0(3)	32.7	43.6	21.9	26.4	23.7(4)	14.1(5)

powder feed rate : 20g/min

Roughly estimated parameters for comparing sprayed condition
Gas energy density : D_E = { (Electricity) − (Loss with cooling water) } ∕ (Gas flow)
Gas velocity : v = (Gas flow) ∕ (cross-section of nozzle orifice)
(electrically open circuit, appearance velocity)

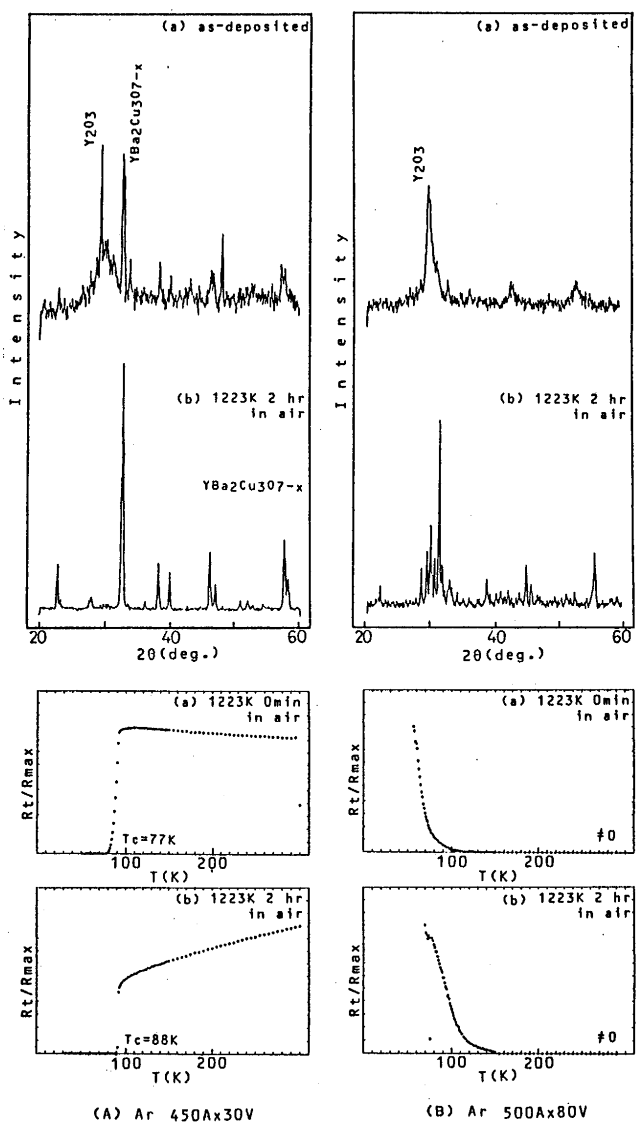

Fig. 2 Effect of plasma power and thermal treatment on XRD patterns and Tc measurement results of coating (superconducting powders).

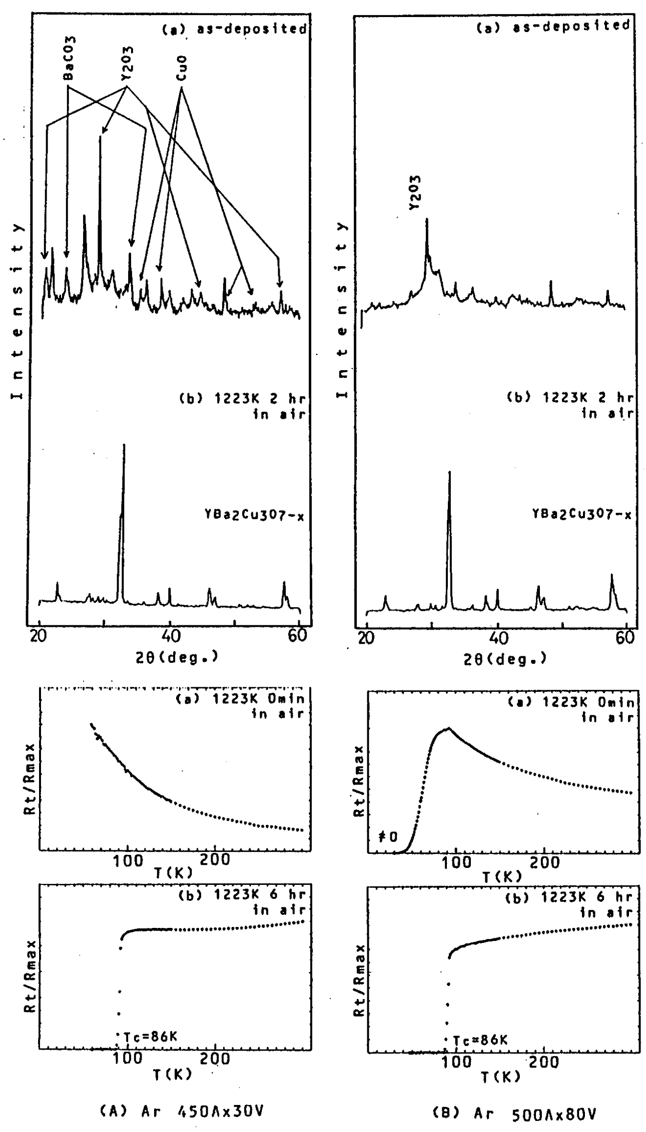

Fig. 3 Effect of plasma power and thermal treatment on XRD patterns and Tc measurement results of coatings (agglomerated powders).

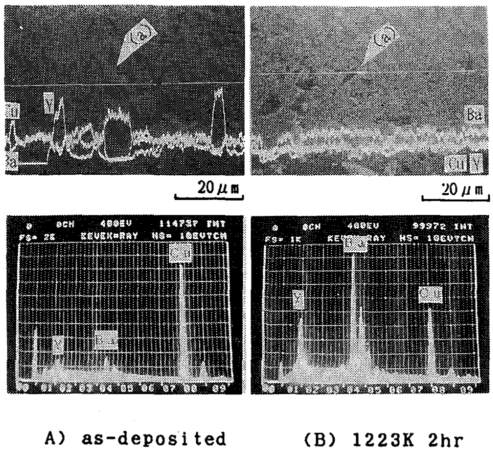

Fig. 4 Results of EDX element analysis of cross section of as-deposited and thermally treated coatings (composite powder).

3.2 Effect of plasma gas on Tc of deposits

In case of superconducting powders, any deposits (as-deposited and thermally treated) did not exhibit $YBa_2Cu_3O_{7-x}$ peak in X-ray diffraction patterns and superconductivity in Tc measurements, when deposits were produced by plasma spraying with both Ar /H_2 and N_2 plasma gas under plasma spraying conditions in Table 1.

From these results it can be considered that the heat supply to the powders during plasma spraying with Ar /H_2 and N_2 gas were more excessively decomposed the powders than that of Ar mono gas plasma spraying.

However, as shown in **Fig. 5**, for the agglomerated powders, Ar /H_2 and N_2 plasma gases facilitated the mutual reaction among oxides during plasma spraying to

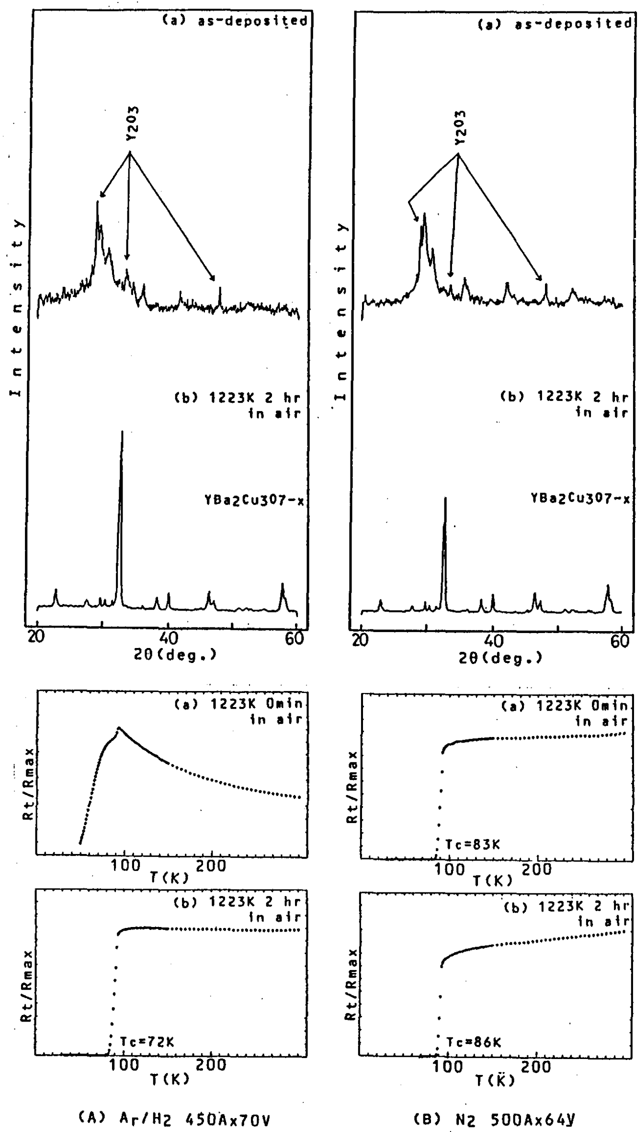

Fig. 5 Effect of plasma gasses and thermal treatment on XRD patterns and Tc measurement results of coatings (agglomerated powders).

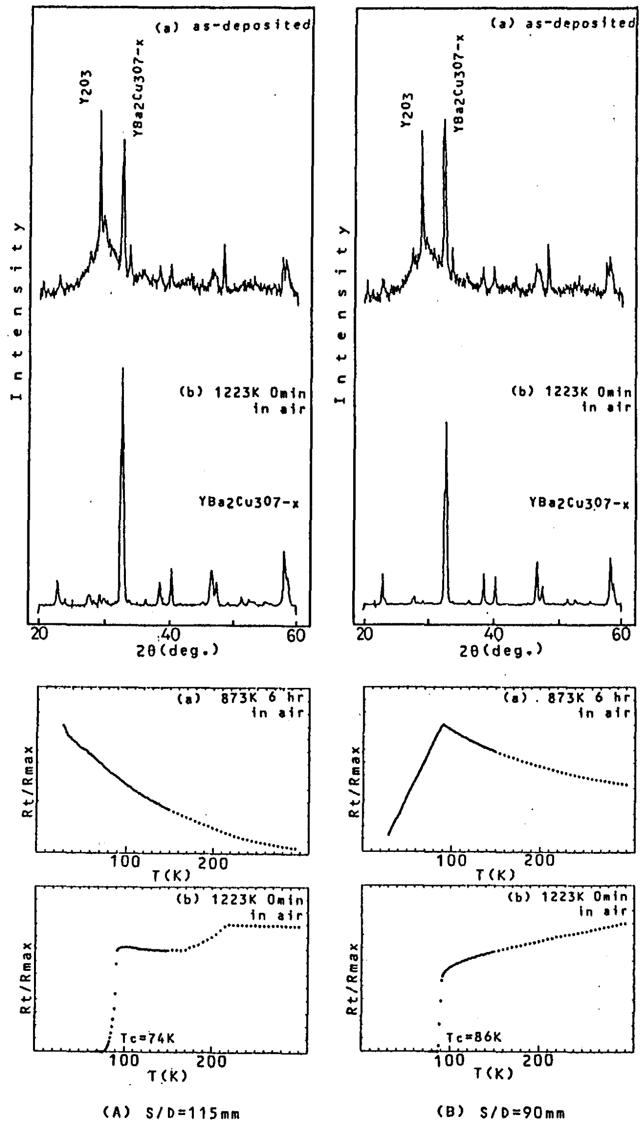

Fig. 6 Effect of gas flows and standoff distance on XRD patterns and Tc measurement results of coatings (superconducting powders).

give the deposits which showed the superconductivity by heat treatment for shorter time, as compared with Ar mono plasma gas as shown in Fig. 3. As making comparison between N_2 and Ar /H_2 gases, N_2 gas was more remarkable to react than Ar/H_z gases because the deposit thermally treated for 0min at 1223K exhibited Tc = 83K.

3.3 Effect of Gas flow rate and standoff distance on Tc of deposits

Above obtained results showed that it was necessary to control heat content of plasma jet in the case of the superconducting powders, in order to suppress decomposition of powders and keep the superconductivity of deposits.

The effect of standoff distance(S/D) on Tc of deposits was examined under plasma spray conditions, where heat content was controlled fully as shown in Table 1. The results were shown in **Fig. 6**. From this figure, it was seen that the decomposition of powders was suppressed more by plasma spraying at shorter distance of 90mm. There was a presence of quite intensitive $YBa_2Cu_3O_{7-x}$ peaks in XRD patterns of both of as-deposited. Therefore, main peak of Y_2O_3 was greater than that of $YBa_2Cu_3O_{7-x}$ for deposits at S/D = 115mm. On the other hand, at S/D=90mm $YBa_2Cu_3O_{7-x}$ peak remained greater than that of Y_2O_3. A reduction of resistance was observed from Tc measurement result of thermally treated deposit at 873K for 6hrs in the case of S/D = 90mm and a resistance-temperature property like a sintered pellet was observed in the result of thermally treated deposit at 1223K for 0min. It may be considered that existence of $YBa_2Cu_3O_{7-x}$ composition in deposits (preventing crystallization of Y_2O_3) through the deposition process facilitates to recover a superconductivity by simple thermal treatment. In other words, keeping particle in plasma jet for shorter time is an effective method of plasma spraying of superconducting powders (Fig. 5).

SEM photographs of surface and fracture surface of deposits obtained at S/D = 90mm in Fig. 6 were shown in **Fig. 7**. These show that as-deposited is not seen as a substantially layered structure constituted with flattened particles, slight melting of deposit was observed by heat treatment at 873K, and crystallized grains fully were grew up by heat treatment at 1223K.

Plasma spraying parameters in this examination are showed in Table 1. For comparing sprayed conditions, roughly estimated parameters of gas energy density(DE) and gas velocity(v) are introduced. In the case of superconducting powders, high Tc after thermal treatment was obtained under the condition of 24J/cc (DE). However at 500Amp×40Volts, Ar/H_2 and N_2, high Tc was not obtained. It may be considered that high gas velocity

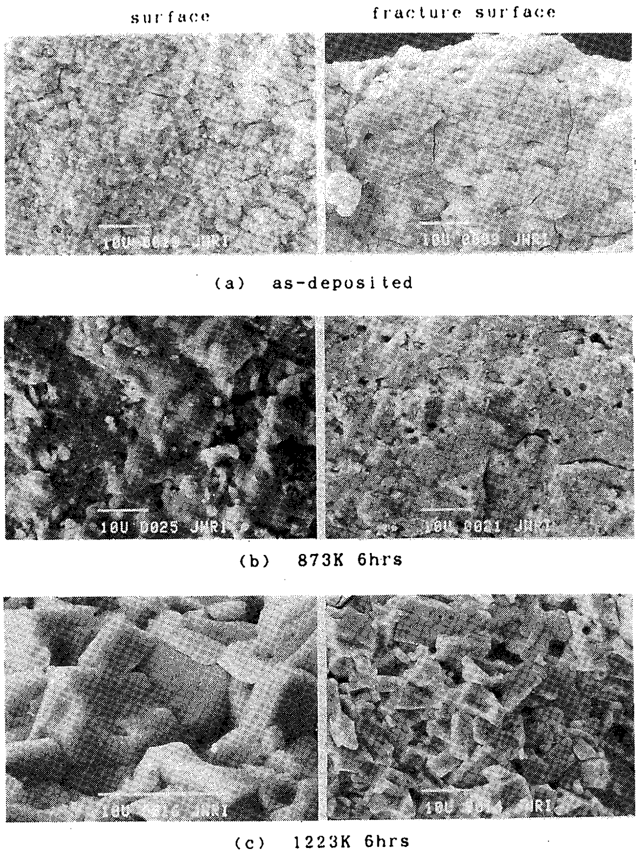

Fig. 7 SEM photographs of coating surface and fracture surface of coating.

is effective for obtaining high Tc deposits in insufficient melting of particles and prevent decomposition of those. On the other hand, high heat content results in a excessively decomposition of particles and no recovery of superconductiveity by thermal treatment. Because high Tc by thermal treatment of a very short period was obtained when deposits were produced by plasma spraying under the conditions of high velocity, low DE and short standoff distance where the decomposition of particles was controlled. In the case of agglomerated powders, high DE is not almost necessary because best result is obtained with N_2 plasma gas when DE is not so great, and all thermally treated deposits for several hours showed reliably a good superconducting property, so that this processing is useful that if deposits are thermally treated at high temperature. In other word, as a result of this examination, it was proved that N_2 gas is more suitable for in-flight composition than Ar or Ar/H_2 gas for air plasma spraying.

4. Conclusion

The effect of plasma spray parameters such as plasma power, plasma gas, gas flow rate and standoff distance on property and structure of $YBa_2Cu_3O_{7-x}$ coatings was examined by using superconducting powders and agglomerated powders of Y_2O_3, $2BaCO_3$ and $3CuO$.

The results obtained were summarized as follows.

(1) In order to obtain superconducting coatings uniformly and easily by post heat treatment, it was important to suppress the decomposition of superconducting powders of $YBa_2Cu_3O_{7-x}$ during plasma spraying. Therefore it was necessary to select plasma spray parameters of lower heat content and adopt lower plasma power, higher gas flow rate and etc.

(2) For the agglomerated powders, it was important to facilitate the mutual reaction among three kinds of oxides of Y_2O_3, Ba_2CO_3 and CuO during plasma spraying. So it was necessary to use N_2 plasma gas in order to increase heat content.

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